

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>H05K 3/02, 3/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/41713</b> <b>(43) International Publication Date:</b> 6 November 1997 (06.11.97)
<b>(21) International Application Number:</b> PCT/US97/07191 <b>(22) International Filing Date:</b> 1 May 1997 (01.05.97)  <b>(30) Priority Data:</b> 60/016,665 1 May 1996 (01.05.96) US 08/846,380 30 April 1997 (30.04.97) US  <b>(71) Applicant:</b> ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). <b>(72) Inventors:</b> FATCHERIC, John, F.; 710 Freedom Street, Holmen, WI 54636 (US). CARBIN, Derek, C.; 10 Blackberry Lane, Bennington, VT 05201 (US). <b>(74) Agent:</b> CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated States:</b> AL, AU, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LK, LR, LS, LT, LV, MG, MK, MN, MW, MX, NZ, PL, RO, RU, SD, SG, SI, SK, TR, TT, UA, UZ, VN, ARIPO patent (GH, KE, I.S, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> NEW METHOD OF FORMING FINE CIRCUIT LINES  <b>(57) Abstract</b>  A new method of forming circuit lines on a substrate by applying conductive metal(s) using copper foil as a carrier. The copper foil is etched away, leaving the conductive metals embedded in the surface of the substrate. A photoresist is used to expose trenches which define the desired circuit and copper is applied onto the exposed conductive metals. The method is particularly suited to manufacturing the outer layers of multi-layer circuit boards.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

NEW METHOD OF FORMING FINE CIRCUIT LINES

Priority is claimed from United States Provisional Patent Application No. 60/016,665 filed on May 1, 1996.

This invention relates generally to methods for producing printed circuit  
5 boards. In particular, it relates to a new method of forming very fine circuit lines.

In the typical production of printed circuit boards, thin copper foil is laminated to an insulating substrate, most often a glass reinforced epoxy resin prepreg, and then that laminate is further processed to convert the copper foil into a circuit pattern by selectively removing portions of the copper by chemical  
10 etching. Such etching is generally satisfactory, but its limitations become apparent whenever finer (narrower) circuit lines are required.

Quite frequently, the copper foil may be treated prior to lamination in order to enhance its ability to bond to the insulating substrate. For purposes of this application, unless otherwise specified, references herein to copper foil shall  
15 be construed as referring interchangeably to both treated and untreated copper foil.

In practice, the etchants do not create vertical sides of the circuit lines. Instead, they tend to etch away too much copper at the top of the line by undercutting the resist and less at the bottom of the line, leaving a somewhat  
20 trapezoidal-shaped circuit line. As a result, the minimum width of the circuit lines is limited by the need to allow for such non-uniform etching. This problem was discussed in US 5,437,914 and it was shown that the shape of the etched circuit lines was affected by the shape of the grain structure of the copper foil. Improved accuracy of etching was to be obtained according to the '914 patent by laminating  
25 the copper foil to the substrate with the "shiny" side down, which is contrary to the conventional practice. An improved etching factor was obtained, indicating that the sides of the circuit lines were more nearly vertical.

Another approach to improving the accuracy of circuit lines is to use thinner copper foils, since they can be etched quickly with less undercutting. However, such foils are not easy to handle. Consequently, it has been proposed to deposit thin layers of copper on supporting sheets which can be removed after the

foil has been laminated to a substrate. One example is found in US Patent 3,998,601 in which a 2-12  $\mu\text{m}$  layer of copper is deposited on a conventionally  
5 thick copper foil (say 35-70  $\mu\text{m}$ ) and separated by a release layer. After laminating the composite foil to a substrate, the supporting copper foil is mechanically stripped away, leaving the thin 2-12  $\mu\text{m}$  foil ready for processing into an electronic circuit. Such a procedure may result in removing portions of the thin foil when the supporting foil is stripped away.

10 The present invention solves the etching problem in a completely different manner. No etching away of the copper foil is used in creating the circuit lines, but instead the circuit lines are electrodeposited onto very thin conductive layers within trenches defined by a resist. The method is particularly advantageous when used to make the outer circuit layers of multilayer circuit boards, but also  
15 may be used for inner layers or one- and two-sided circuit boards.

#### SUMMARY OF THE INVENTION

In one aspect, the invention is a new method of forming very narrow circuit lines on a non-conductive substrate by applying copper over a thin conductive layer in regions defined by a cured photo resist. This is made possible  
20 by applying a thin layer of a conductive metal, metals, or alloys to the non-conductive substrate. The conductive metal, metals, or alloys are applied to a sheet of copper foil and then the copper foil is laminated to a substrate, with the conductive metal layer between the copper and the substrate. If the copper foil is treated to enhance its ability to bond to the substrate, the conductive metals may  
25 be applied to the copper foil either before or after such treatment. During processing of the circuit board, the copper foil is etched away, leaving the thin conductive metals in place. A photoresist is then applied, imaged, and cured. The uncured resist is removed, thus defining the region or "trench" in which the circuit lines are wanted. Since the conductive layer is now exposed, it is possible to selectively apply the circuit lines in those regions. Finally, the cured photoresist is removed and the conductive metal layer which has been exposed is removed by chemical etching, leaving the finished circuit.

It will be understood by those skilled in the art that the copper foil and

5       conductive metals may be applied to the respective surfaces by any conventional method including, but not limited to, electrolytic deposition, chemical vapor deposition, electroless deposition and sputtering.

          In a preferred embodiment, electroless copper plating is used to cover the conductive metal layer before electrodepositing the circuit lines.

10                               DESCRIPTION OF THE DRAWINGS

          Figure 1 is a block diagram of the process of the invention applied to multi-layer circuit boards.

          Figure 2 is a block diagram of the prior art process for multi-layer circuit boards.

15       Figure 3 illustrates cross-sectional view of conventional circuit lines compared with those of the invention in multi-layer circuit boards.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

          The invention comprises a new process of forming a printed circuit board and the board which results from that process. The process employs conventional  
20       procedures, but has significant advantages, particularly in that the circuit lines are more accurately defined than in conventional processing. Thus, finer circuit lines can be produced, which can be more densely packed on the board.

          It is conventional practice to electrodeposit metals onto copper foil. For example, in the '914 patent a nodular deposit copper is formed on the shiny (the  
25       smooth) side of copper foil in order to roughen it and improve its adhesion to insulating substrates. In co-pending commonly assigned US patent application 08/517,321 a fine deposit is placed on copper foil in order to improve adhesion, although the measured roughness of the foil is not changed. A similar approach is disclosed in US 5,482,784.

30       In a series of patents assigned to Ohmega Electronics (e.g., US 4,808,967) a technique for creating resistors on the surface of a printed circuit board is discussed. It starts with the electrodeposition of a layer of nickel-phosphorus on the surface of copper foil, which is then laminated to an insulating substrate. Rather than acting as a typical conductive layer, the nickel-phosphorus layer is exposed by selective etching away of the covering copper where resistors are

5       needed in the circuit design. The remaining copper layer is turned into the conductive circuit lines by conventional etching procedures.

          The process of the present invention is clearly different from conventional circuit board processing in which the circuit lines are formed by selectively etching copper away. As explained above, chemical etching has inherent  
10       limitations which become particularly troublesome as circuit lines become narrower and their pitch closer. The new process of the invention deposits the circuit lines directly into spaces created by the use of a photoresist, which leaves open trenches to be filled by electrodeposition of copper. This is made possible by the conductive layer which remains on the surface of the substrate once the  
15       covering copper foil carrier has been removed. The process of the invention is also different from that of the Ohmega process in which the layer at the surface of the substrate serves as a resistor.

          The process is shown in the block diagram of Figure 1 as applied to the outer layers of a multi-layer board. In the first step, copper foil is passed through  
20       a bath of soluble compounds of the conductive metals and they are electrodeposited to a thickness of about 0.2 to 5  $\mu\text{m}$  on one surface of the foil, either the matte or shiny side. As previously identified, either before or after application of the conductive metal, the copper foil may be given a treatment (such as nodular copper) to improve its adhesion to the insulating substrate. The  
25       metals or alloys may be tin, nickel, tin-zinc, zinc-nickel, tin-copper and others, provided that they are resistant to the etchant used to remove copper during a subsequent step. The conditions of the electrodeposition process are typical of those used commercially to provide protective metal coatings on copper foil.

          In the second step the coated copper foil is laminated to an insulating substrate, such as the commonly used glass reinforced epoxy resins, using conventional techniques and with the conductive metals next to the substrate.

          The next step is to etch away the copper foil, leaving the thin layer of  
5       conductive metal embedded in the surface of the substrate. For this purpose, the etchant is selected from those which will remove copper, but not the metals of the conductive layer to a significant extent. An example of such etchants is

ammoniacal cupric chloride. Thin copper foils have been applied in the past from aluminum supporting layers, with the aluminum being etched away in a similar manner. It is an advantage of the present process that copper is recoverable and that contamination with dissolved aluminum is avoided, which would occur if aluminum were to be substituted for copper in the process of the invention. Once the copper has been etched away the conductive metal (or alloy) layer is exposed and ready for application, imaging, and curing of the photoresist.

In the process of this invention, the uncured photoresist is removed to expose trenches which will form the circuit lines. It will be evident to those skilled in the art that cured photoresist will more accurately define the circuit lines and that the copper which fills the trenches will more closely approach the ideal rectangular shape than would circuit lines formed by etching away copper in exposed areas. This means that finer circuit lines can be made because their shape is not determined by an etching process. Consequently, rather than 4 mil (100  $\mu\text{m}$ ) lines and spaces, the new process permits reducing the lines and spaces to about 1 mil (25  $\mu\text{m}$ ).

The copper is electrodeposited using conventional procedures such as are often used to plate copper onto the outside of multilayer circuit boards. It is possible to do this when the thin layer of metals embedded in the surface of the substrate is sufficiently conductive. If not, electroless plating of copper can be used to facilitate the electrodeposition of the circuit lines. The copper can be built up in thickness as desired, up to the height of the photoresist which defines the shape of the trenches. Conventional electrodeposition conditions will be used.

At this point, the circuit lines have been formed. What remains is to remove the photoresist by conventional means, following which the conductive metal layer which has been exposed is removed by using an etchant, such as acid cupric chloride or sulfuric peroxide.

It will be readily apparent to those skilled in the art that the specific steps of the invention (*e.g.* those illustrated in Figure 1) may be performed in any order that is commercially practicable. In particular, the steps subsequent to applying the

conductive metal to the laminate may be performed in whatever method is feasible for the operator.

10       The invention has particular value in making the outer layers of multi-layer circuit boards. Multilayer circuit boards generally have holes connecting outer with inner layers which are electroless plated with copper and then the circuit lines are formed by electroplating. The typical procedure is shown in the block diagram of Figure 2. Copper foil is laminated with an intervening layer of  
15       pregreg to the inner circuit layers, but is not etched away. Electroless plating is used to deposit copper over the foil and down the holes which connect the layers. Then, a resist is applied and the copper circuit lines are electrodeposited. At this point, the excess copper foil must be removed by etching. However, the circuit lines and the plated holes must be protected by a step of electrodepositing a  
20       resistant metal, such as tin. Then the resist can be removed and the exposed copper foil etched. It can be appreciated that such a step causes the sides of the circuit lines not protected by the tin to be attached also. In the present invention, tin need not be applied since it is only necessary to remove the thin conductive layer, which can be accomplished very quickly. Importantly, the substantial costs  
25       of disposing of solutions needed for applying and removing the tin layer are avoided.

      Figure 3 illustrates the circuit lines formed in the outer layers of multi-layer circuit boards by conventional etching processes, compared to the essentially rectangular line formed using the process of the invention. The circuit  
30       lines of the prior art are severely undercut by the need to etch away copper foil after the circuit lines are formed (the top being protected by the tin coating).

      The process of the invention makes possible more accurate production of circuit lines and thus, the circuit designer does not have to compensate for the inaccuracy inherent in the formation of circuit lines by etching. This means the resulting circuit can be smaller and more compact. The process uses techniques  
5       which are familiar to circuit board manufacturers and does not involve large changes in technology. In fact, it is expected that the production processes will be simplified when the process of the invention is adopted.



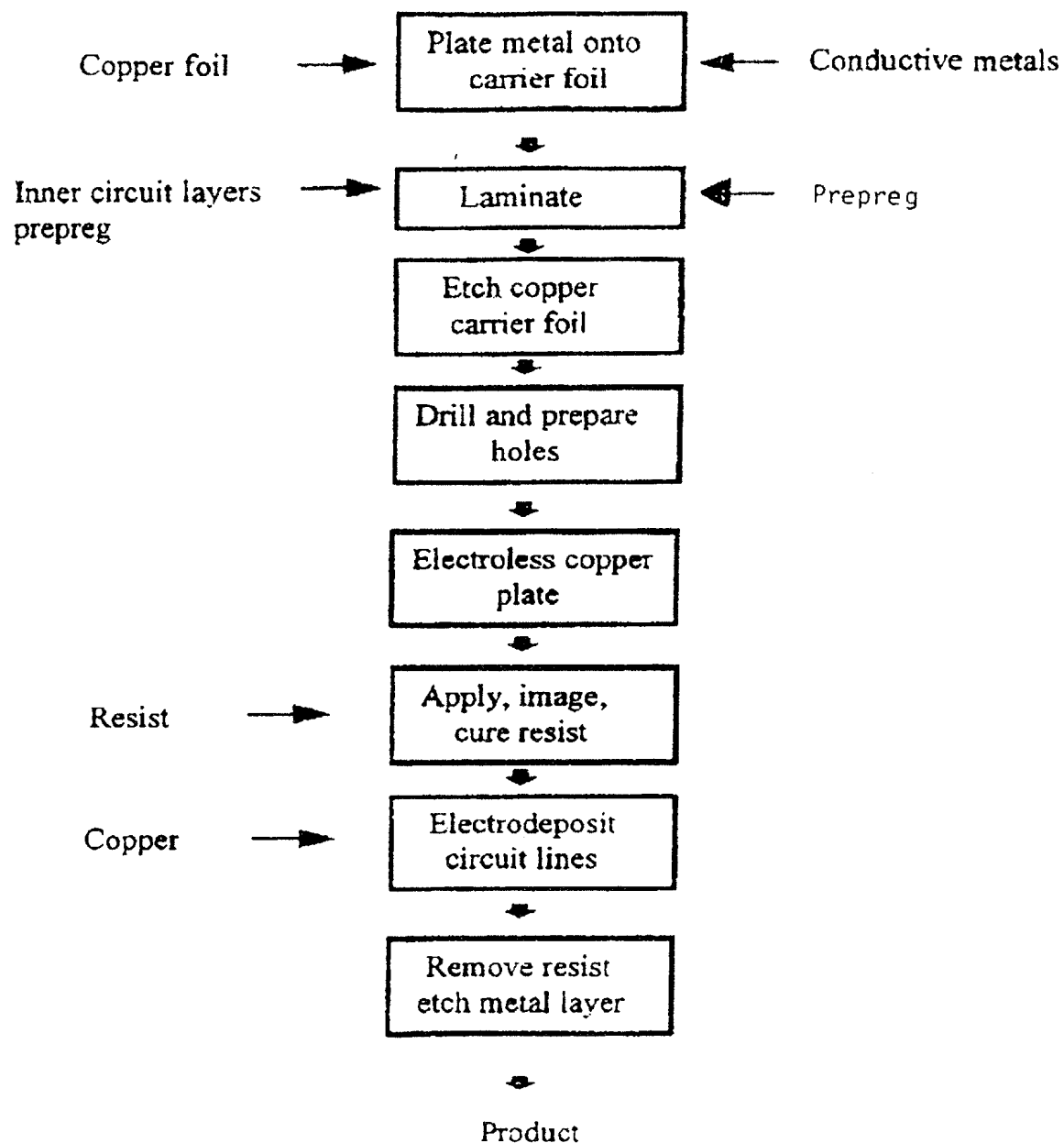
CLAIMS

1. A method of forming circuit lines comprising the steps of
  - (a) applying on a sheet of copper foil a layer of conductive metals resistant to etchants used to remove copper;
  - 5 (b) laminating the conductive metal containing sheet of copper foil of (a) with a prepreg or a film substrate;
  - (c) etching away the copper foil from the laminate produced in (b) and leaving the conductive metal(s) embedded in the surface of said prepreg or film substrate;
  - 10 (d) applying, imaging, and curing a photoresist over the conductive metal(s) and substrate produced in (c);
  - (e) removing the uncured photoresist of (d) leaving trenches having exposed conductive metal(s);
  - 15 (f) applying copper onto the exposed conductive metals of (e) to produce circuit lines;
  - (g) removing the cured photoresist of (d) to expose conductive metal(s) and etching away the exposed conductive metals, thereby producing a circuit on said substrate.
2. The method of Claim 1 wherein said layer of conductive metal is 0.2 to 5  
20  $\mu\text{m}$  thick.
3. The method of Claim 1 wherein the conductive metals are applied to the copper foil by electrolytic deposition.
4. The method of Claim 1 wherein the conductive metals are applied to the copper foil by chemical vapor deposition.
- 25 5. The method of Claim 1 wherein the conductive metals are applied to the copper foil by electroless deposition.
6. The method of Claim 1 wherein the conductive metals are applied to the copper foil by sputtering.
7. The method of Claim 1 wherein said conductive metals are selected from the group consisting of tin, nickel, tin-zinc, zinc-nickel, and tin-copper.

8. A laminate comprising a substrate on which circuit lines are formed by the method of Claims 1, 2, 3, 4, 5, 6 or 7.
- 5 9. The laminate of Claim 8 wherein said substrate is the inner layers of a multi-layer circuit board.
10. A copper foil for use in making circuit boards by the method of Claims 1, 2, 3, 4, 5, 6 or 7.

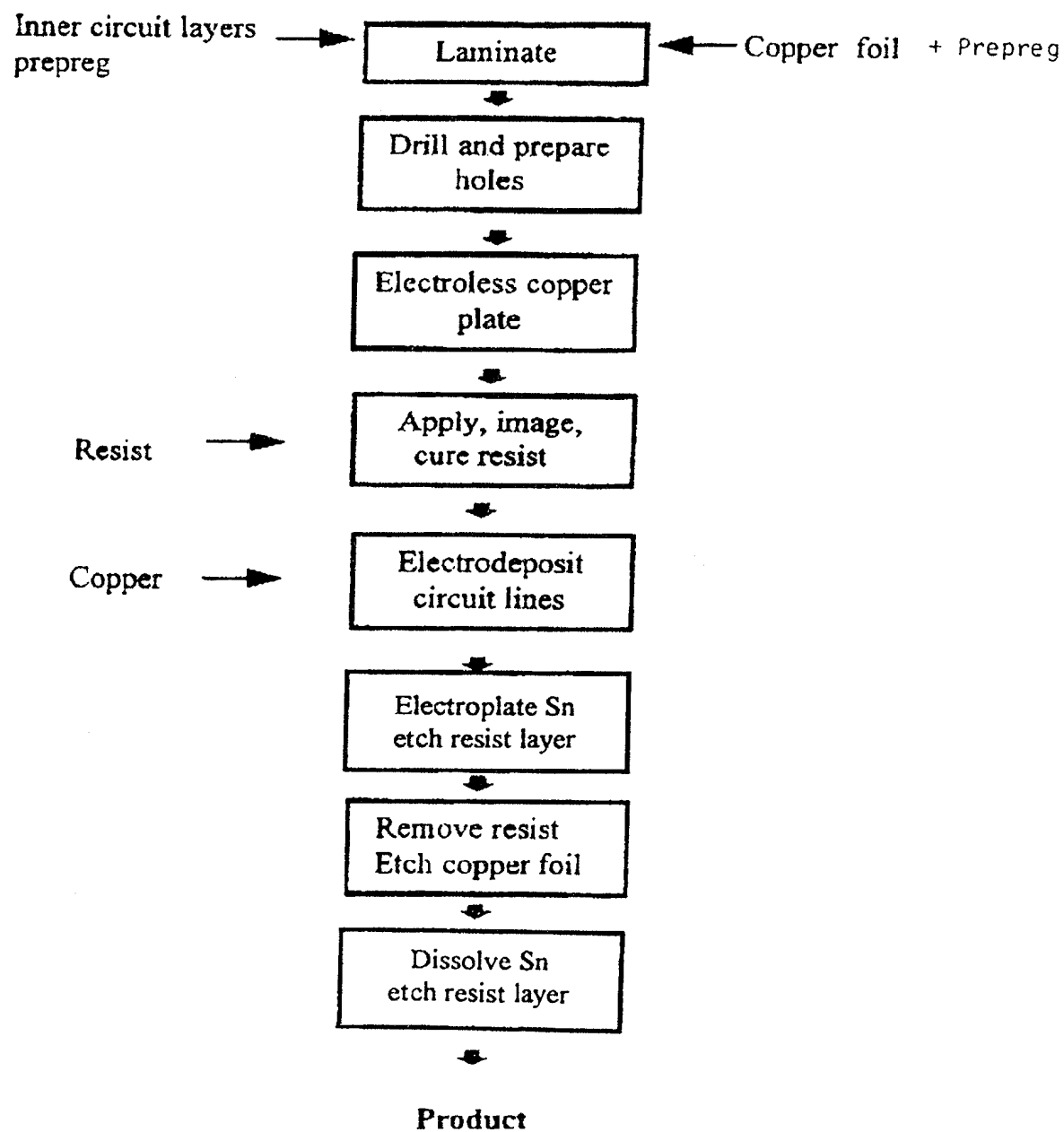
1 / 3

Figure 1

**INVENTION**

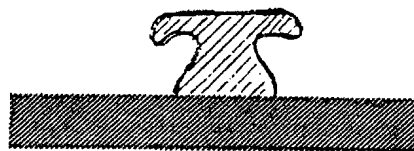
2 / 3

Figure 2  
PRIOR ART

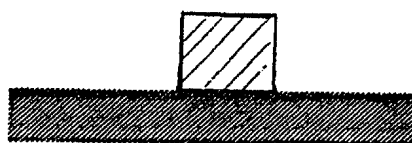


11

FIGURE 3



Prior Art



Invention

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/07191

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 H05K3/02 H05K3/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 017 271 A (WHEWELL ET AL.) 21 May 1991 see the whole document	1-3,5-8, 10
X	--- PATENT ABSTRACTS OF JAPAN vol. 13, no. 371 (E-807), 17 August 1989 & JP 01 124286 A (HITACHI CHEM CO), 17 May 1989, see abstract	1,7,8,10
A	--- PATENT ABSTRACTS OF JAPAN vol. 13, no. 181 (E-750), 27 April 1989 & JP 01 008694 A (HITACHI CHEM CO), 12 January 1989, see abstract -----	1,5,7,8, 10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

Date of the actual completion of the international search

13 August 1997

Date of mailing of the international search report

04 -09- 1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Mes, L

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inventor's Application No  
PCT/US 97/07191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5017271 A	21-05-91	AU 649666 B	02-06-94
		AU 7653791 A	17-03-92
		DE 69121183 D	05-09-96
		DE 69121183 T	05-12-96
		EP 0497925 A	12-08-92
		HU 62042 A,B	29-03-93
		JP 5504658 T	15-07-93
		WO 9203599 A	05-03-92
-----			